Development and Analysis of Original UNIFAC-CI and Modified UNIFAC-CI Models for Predictions of VLE and SLE Systems

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Prediction of properties is important in chemical process-product design. Group-contribution (GC) methods provide useful tool but there is a need to validate and improve their accuracy when complex chemicals are present in the mixtures. In accordance with that, a combined GC and atom connectivity approach that is able to extend the application range of property models has been developed for mixture properties. This so-called GC^{Plus} approach is a hybrid model which combines GC and valence connectivity indices (CI). The main idea is the use of CI to describe the molecular fragmentation that relates properties, the molecular interactions with the molecular structures. One established GC method is the UNIFAC model to predict liquid phase activity coefficients. The needed values of the group interaction parameters (GIPs) are obtained by fitting phase equilibrium data. There are many gaps in the UNIFAC parameter table due to lack of data. Alternative to performing measurements, values of the missing GIPs, can be predicted through the GC^{Plus} approach. The predicted values for the GIPs are then used in the UNIFAC model to calculate activity coefficients. In this work, the model parametersfor using the GC^{Plus} approach to the original UNIFAC and Modified (Dortmund) UNIFAC have been regressed against vapor-liquid equilibrium (VLE) data and simultaneously against VLE and solid-liquid equilibrium (SLE) data for groups formed by C, H, O, N, Cl and S atoms. Initially the VLE data used to regress those parameters are checked using a quality assessment algorithm which combines four widely used consistency tests (Herington, Van Ness, Point/Differential and Infinite Dilution tests) and also a check on the consistencies of the data with the pure component vapor pressures. The overall quality factors, Q_{VLE} obtained for each dataset indicate the quality of each datasets and can then be used as weighting factors, in the objective function for the parameter regression with VLE data (and with SLE data). The performance of the CI-models using parameters regressed against VLE data and simultaneously against VLE and SLE data are compared in terms of the uncertainties of the parameters regressed against the predicted properties and the accuracy of the predictions. In addition, the model performances are compared with their reference UNIFAC models.